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SEVENTH QUARTERLY REPORT

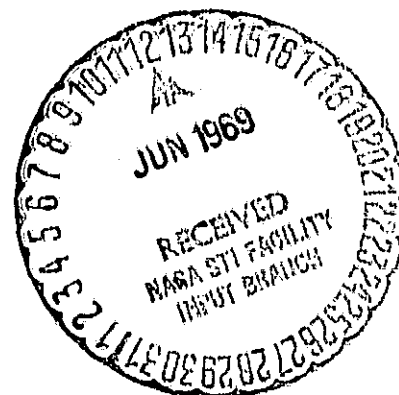
SECONDARY ZINC-OXYGEN CELL FOR SPACECRAFT
APPLICATIONS

(23 December 1967 - 23 March 1968)

CONTRACT No. NAS-5-10247

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND



Prepared by

UNION CARBIDE CORPORATION
CONSUMER PRODUCTS DIVISION
RESEARCH LABORATORY-PARMA, OHIO

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APPROVED BY:



R. A. Powers, Director

CONSUMER PRODUCTS DIVISION
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ABSTRACT

Zinc-oxygen cells employing anodes made from asbestos fiber bonded zinc oxide formulations delivered 124 and 144 cycles on a 2-hour discharge/4-hour charge regime at 25°C. Discharge was to 0.8 volt at a current density of 31 mA/cm². This corresponds to a 60 percent zinc depth of discharge based upon the weight of zinc metal present after electroforming. Similar cells have progressed to 11, 21, and 23 cycles at 0°, 25°, and 40°C, respectively, on a 24-hour discharge/24-hour charge cycle. This represents a 75 percent zinc discharge depth based upon the weight of zinc metal present after the electrodes are initially electroformed.

Zinc-oxygen cells employing zinc powder-gel type anodes delivered 176 cycles on a 2-hour discharge/2-hour charge regime at 25°C. Discharge was to 0.8 volt at a current density of 22 mA/cm². This corresponded to a 17 percent zinc depth of discharge based upon the weight of the zinc powder.

The electrolyte expansion chambers at the top of the unit cell have been redesigned so as to permit cell cycling at essentially constant electrolyte levels.

* * * *

INTRODUCTION

Zinc-oxygen rechargeable unit cells employing Union Carbide zinc gel-type anodes delivered over 350 cycles at a current density of 11-12 mA/cm² to a depth of 12-14 percent of the theoretical ampere-hour equivalents of zinc present in the anodes. Continued cycling with good voltage regulation was also demonstrated after recharging from occasional complete discharge of the anode. The performance of such cells has been reported in the fourth and fifth quarterly reports.

Failures associated with 70-80 percent anode slump due to shape change were not uncommon after 50-60 cycles in cells employing this anode structure when they were repeatedly discharged at a current density of 22-25 mA/cm² to 25-30 percent depth. However, slumping was retarded and cycle life was extended from 50-60 cycles to 176 cycles on anodes discharged at a current density of 22-25 mA/cm² when the anodes were of sufficient capacity that the ampere-hour output per discharge was equivalent to 13-17 percent of the total zinc capacity.

Investigation of anode plates fabricated from zinc oxide with various admixtures was incorporated into the zinc-oxygen rechargeable unit cell test program. This investigation was aimed toward minimizing anode shape change and extending the cycle life of rechargeable zinc-oxygen unit cells when subjected to repeated deep discharges and higher discharge current densities. Anodes were fabricated from formulations designated ZnO#1, ZnO#10, and ZnO#19. These formulations are mixtures of ZnO and asbestos fibers. ZnO#10 also contains copper and zinc powders. Since these anodes were fabricated entirely or partially in the discharged state, electroformation cycling was required. Anodes fabricated from ZnO#1 and ZnO#10 mixes delivered 144 and 120 two-hour discharge/4 hour charge cycles, respectively, when discharged at 25°C at a current density of 31 mA/cm², to a depth of 60 percent of the theoretical ampere-hour equivalents of zinc present after electroforming. Cells employing anodes fabricated with ZnO#19 formulation are still cycling on 24-hour discharge/24-hour charge modes at 25° and 40°C at constant current discharge of 0.32 amperes.

A problem with electroosmosis was encountered when these ZnO unit cells were cycled on a 2-hour discharge/4-hour charge schedule. These cells were discharged between 2.5 to 3.0 ampere-hours. The charge was balanced to the discharge. This problem was eliminated by constructing a channel to connect the electrolyte reservoirs situated above the negative and positive compartments in the cell enclosure.

Also, cycling of cells employing ZnO anodes at 25° and 40°C on a 24-hour discharge/24-hour charge schedule has progressed to 23 and 21 cycles, respectively. Discharge depth was to 75 percent of the theoretical ampere-hour equivalents of zinc present after electroforming. A cell that had been previously cycled for 10 cycles on a 2-hour discharge/4-hour charge schedule at 40°C delivered 11 cycles at 0°C.

Evaluation of the American Cyanamid LAB-40 oxygen electrode as a means of eliminating the separate charging electrode was continued during this report period. Continuous back pressure applied to the gas side of the electrode retards leakage through the electrode; however, deterioration of the electrode during cell operation is still a problem.

DISCUSSION

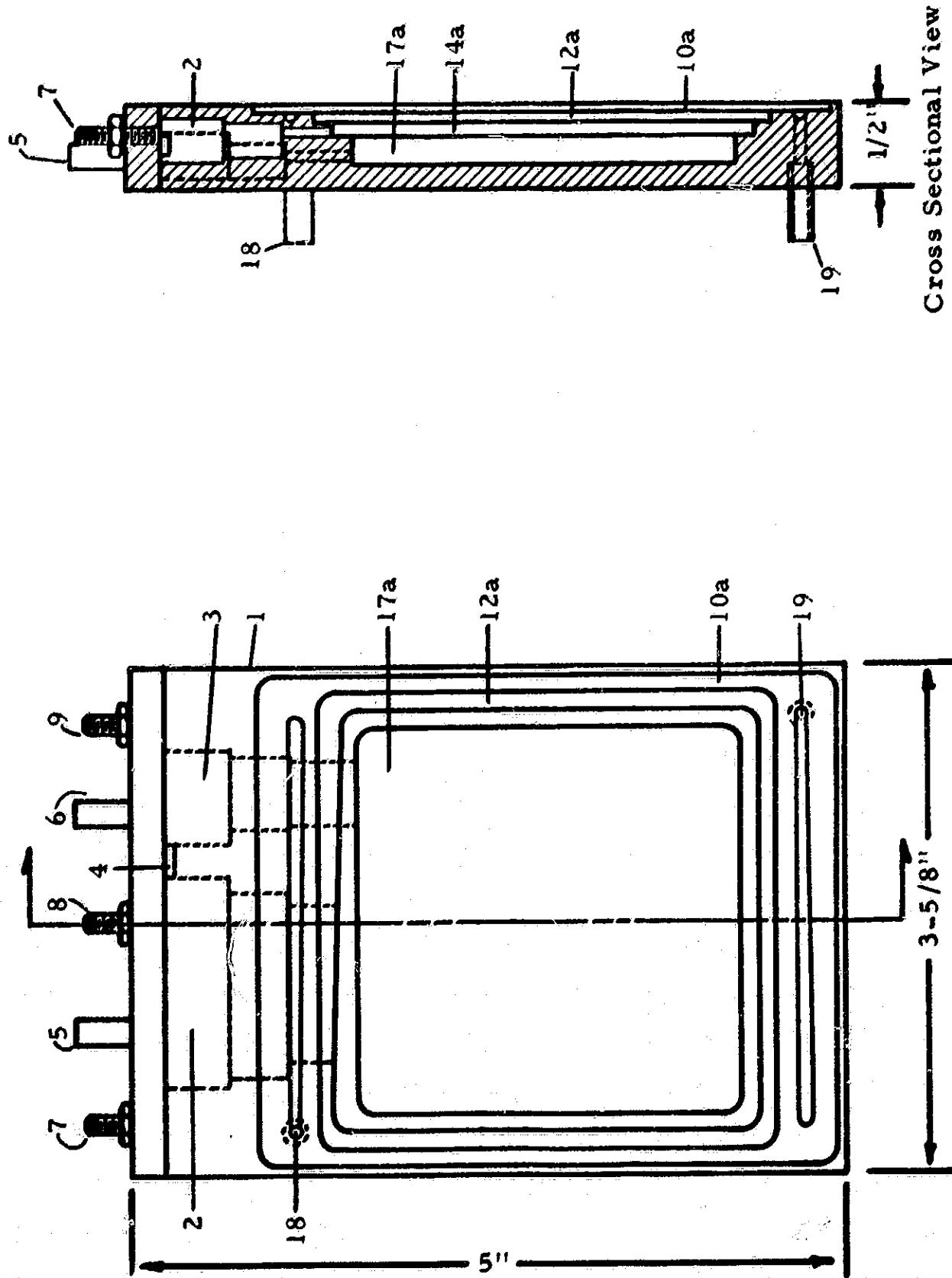
A. Experimental Unit Cell Construction

A channel was constructed to connect electrolyte reservoirs which are situated above and communicate with the anode and cathode compartments. Construction of the channel was necessary to equilibrate the electrolyte levels in the respective compartments as they were affected by the electroosmotic transport of water across the membrane separator during cell operation. A balance in the electrolyte levels of the respective compartments was maintained by flow of electrolyte from the higher electrolyte compartment across the channel to the other one.

Figure 1 shows a front and cross sectional view of the unit cell enclosure without the cell components. A cutaway and cross sectional view of the unit cell enclosure with cell components is presented in Figure 2. Figure 3 shows a front and oblique view of the complete unit cell.

FIGURE 1

FRONT AND CROSS SECTIONAL VIEWS OF A
ZINC-OXYGEN RECHARGEABLE EXPERIMENTAL UNIT CELL ENCLOSURE



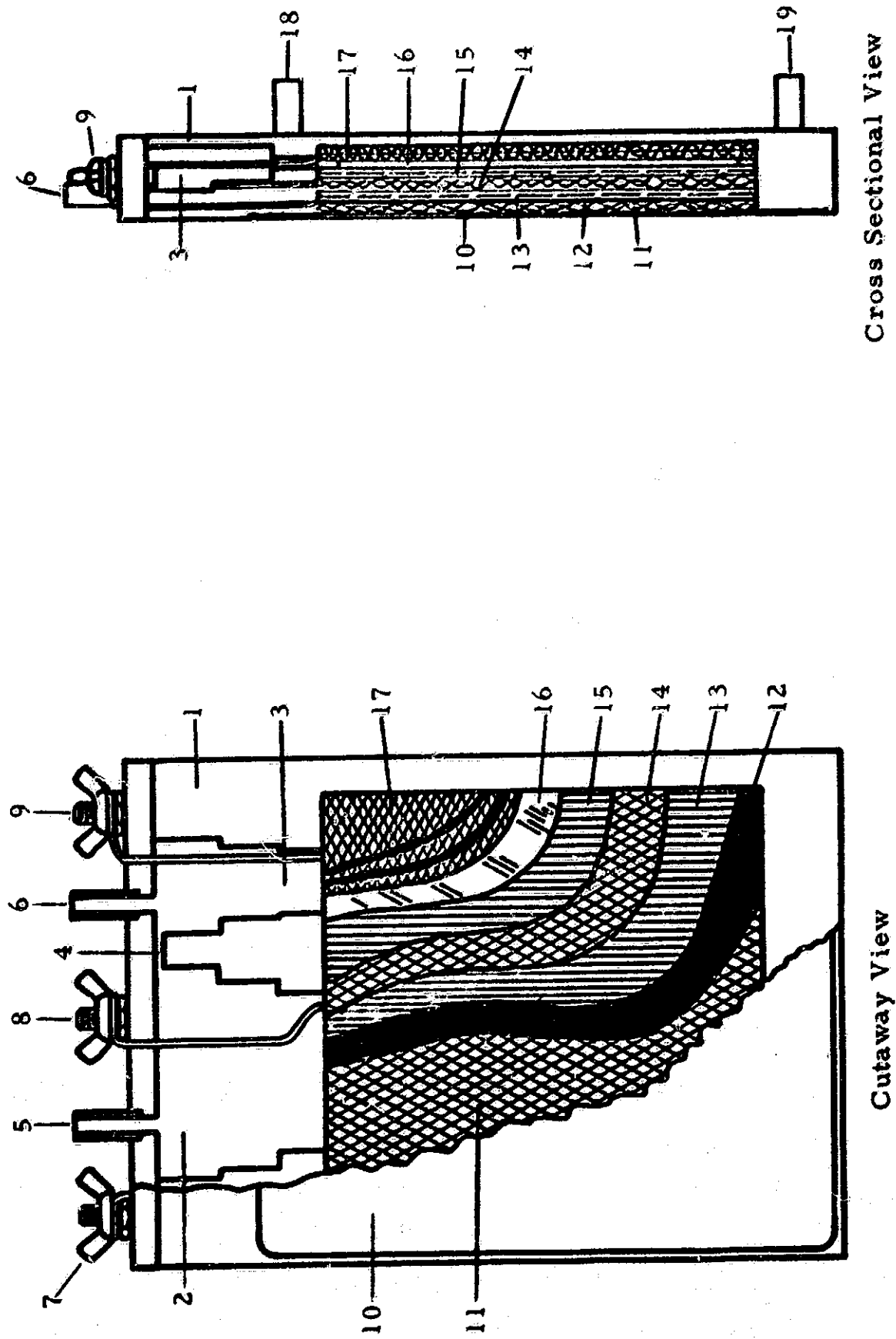
Front View

See Page 6 for Legend.

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FIGURE 2

CUTAWAY AND CROSS SECTIONAL VIEWS OF
ZINC-OXYGEN RECHARGEABLE UNIT CELL

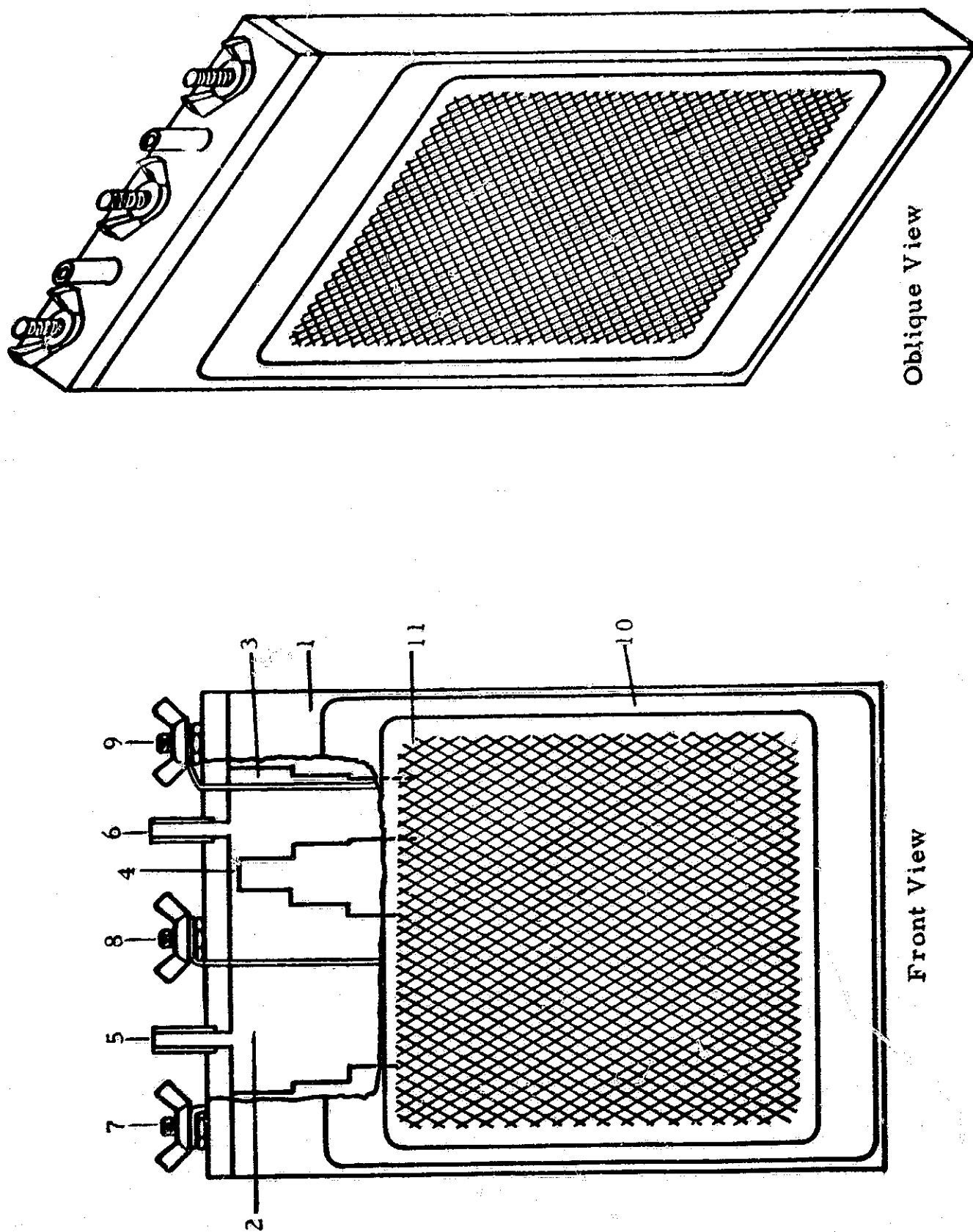


See Page 6 for legend.

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FIGURE 3

FRONT VIEW AND OBLIQUE VIEW OF RECHARGEABLE ZINC-OXYGEN UNIT CELL



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See Page 6 for legend.

LEGEND FOR FIGURES 1, 2, AND 3

1. LUCITE case.
2. Electrolyte reservoir above the positive compartment.
(Positive compartment houses both the oxygen electrode and the charging electrode.)
3. Electrolyte reservoir above the negative compartment.
(Negative compartment houses the zinc electrode)
4. Channel connecting the electrolyte reservoirs above the positive compartment and the negative compartment. (Allows electrolyte to flow from one compartment to the other when levels rise due to electroosmosis.)
5. Gas exit tube above positive compartment.
6. Gas exit tube above negative compartment.
7. External lead to oxygen electrode (only in the electrical circuit during discharge).
8. External lead to charging electrode (only in the electrical circuit during charge).
9. External lead to zinc electrode (in the electrical circuit during both charge and discharge).
10. LUCITE backing plate.
- 10a. Step for LUCITE backing plate.
11. Gas spacer.
12. Oxygen Electrode (2.7" x 2.7" x 0.022").
- 12a. Positive compartment.
13. Vertically positioned vinyl spacers.
14. Charging electrode (2.7" x 2.7" x 0.020").
15. Vertically positioned vinyl spacers.
16. Separator system: (a) PERMION 1770C, (b) VISKON VINYLON, (c) PELLON
17. Zinc Electrode (3" x 3" x 0.120").
- 17a. Negative compartment.
18. Oxygen inlet tube.
19. Oxygen outlet tube.

B. Description of Electrodes

1. Oxygen Electrodes

Construction of three-electrode cells employing Union Carbide thin "fixed-zone" oxygen electrodes with separate charging electrodes and two-electrode cells employing American Cyanamid LAB-40 oxygen electrodes is now in progress. A complete characterization of three-electrode cells employing anodes fabricated from a zinc oxide formulation was initiated during this report period. Investigation of the American Cyanamid LAB-40 oxygen electrode aimed toward developing a two-electrode cell will also be continued.

To date, the problem of deterioration of the LAB-40 oxygen electrode during cell operation has not been solved. However, oxygen pressure continuously applied to the gas side of this electrode helps to reduce electrolyte leakage through the electrode. The optimum back pressure has yet to be established. Both LAB-40 and thin "fixed zone" oxygen electrodes are now being observed for wet-stand time-to-leakage as a function of continuously applied back pressure. The electrodes under observation, however, are not under operating conditions. The test simulates shelf conditions after activation with electrolyte.

Black discoloration across the top of the zinc electrode, accompanied by profuse gassing at this electrode occurred after three or four cycles in all cells employing American Cyanamid LAB-40 oxygen electrodes that were contained in enclosures incorporating the cross channel modification.

Apparently, platinum from the LAB-40 oxygen electrode dissolved in the electrolyte, migrated from the cathode compartment through the inter-connecting channel to the anode compartment, and formed a gassing couple with the zinc. When gassing occurred during discharge, a corresponding reversal of cell voltage would occur. X-ray fluorescence examination of the anodes removed from these cells substantiated the presence of platinum.

This problem, along with others associated with the use of the LAB-40 oxygen electrode, could prohibit its ultimate use in the unit cell. However, efforts involving its use will be continued, at least for the time being.

Based on the work of others, there is some evidence of the utility of negatives larger than positives in retarding anode slump due to shape change. To investigate this concept, the active area of the oxygen electrodes to be used in a final characterization study was reduced from 3 x 3 inches to 2.7 x 2.7 inches so that the 3 x 3 inch anode was 0.6 inch larger than the cathode on all sides. These cells will be evaluated by cycling.

The polarization characteristics of the thin "fixed-zone" electrode indicate that it is capable of operating at the higher current density imposed on it as a result of such a reduction in active area with very little, if any, change in voltage. The LAB-40 oxygen electrode is also capable of operating under these conditions until the problems associated with progressive cycling of this electrode arise.

2. Zinc Electrodes

Anode slump in the amount of 70-80 percent due to shape change occurred by 50-60 cycles when the total output per 2-hour discharge of cells employing 10 ampere-hour zinc gel anodes was 2.5-3.0 ampere-hours, or 25-30 percent of the theoretical ampere-hour equivalents of zinc present in the anodes. These zinc gel anodes consist of a mixture of zinc powder in a carboxymethylcellulose gel. The cells employing these anodes were cycled on a 2-hour discharge/4-hour charge schedule. The average discharge current density was 22 mA/cm². The average charge current density was 11 mA/cm². It was demonstrated that anode slump due to shape change could be retarded and cycle life extended on these anodes if they were cycled on an identical time schedule at identical current densities to a discharge depth of 13-17 percent. Of course, the ampere-hour capacity of the anodes had to be changed to permit the variation in discharge depth.

Anodes of identical structure contained 15 and 20 ampere-hours of total zinc capacity. The cycling schedule and the cycling current densities were identical to those with the cell employing 10 ampere-hour anodes. However, a discharge to 2.5-3.0 ampere-hours output in two hours on these cells was equivalent to 13 and 17 percent of the theoretical ampere-hour equivalents of zinc present in the anodes. Unit cells employing these anodes delivered 176 cycles. A threefold extension of cycle life was realized from a 50 percent increase in zinc capacity.

In addition to the investigation involving zinc gel anodes described above and in previous reports, an investigation involving other zinc anode structures was initiated. The other structures investigated were zinc oxide with various admixtures. The investigation of these anode structures was aimed toward minimizing anode shape change and extending the cycle life of zinc-oxygen rechargeable unit cells when subjected to repeated deep discharges and higher discharge current densities.

Rechargeable anode plates were fabricated from three zinc oxide formulations. The formulations were designated ZnO#1, ZnO#10, and ZnO#19. The constituents of the respective formulations were as follows:

Constituents	ZnO#1	*ZnO#10	ZnO#19
	Percent by Weight		
ZnO (Fisher A. C. S. grade)	83.1	43.0	83.1
HgO (Fisher Reagent grade)	4.0	---	4.4
Asbestos Fibers (fuel cell grade)	5.2	1.5	5.2
Distilled H ₂ O	7.7	---	---
Cu Powder (18 μ)	---	21.5	---
Zn #1205 (New Jersey Zinc)	---	21.5	---
Hg (redistilled)	---	3.4	---
0.1N KOH (Fisher A. C. S. grade)	---	9.1	---
35% KOH + 5% ZnO	---	---	7.3
Total	100.0	100.0	100.0

* Copper, zinc, mercury, and 0.1 N KOH were mixed prior to adding the other constituents. The result was a heavy amalgamated mass with sufficient mercury available to amalgamate the zinc formed during the initial charge. The copper powder also served as a conductive medium.

The following procedure was followed in fabricating anodes from the above mix formulations: Half of the amount of mix needed to fabricate an anode of a desired total capacity (15 ampere-hours in this case) was uniformly spread out in a preformed 3 x 3 inch expanded silver envelope. A 2¹⁵/₁₆ x 2¹⁵/₁₆ inch expanded silver grid was centrally situated and spot welded across the top

to the silver envelope. This centrally situated grid was pressed onto the mix. The remainder of the mix was uniformly spread out over the centrally situated grid, after which the silver envelope was folded over to enclose the mix. These anodes were molded into 3 x 3 inch x 0.115 inch plates. The anode mass makes bilateral-symmetrical contact with the expanded silver collectors. Since these anodes were fabricated in the discharged state, a formation cycle* was required. Anodes that were subsequently cycled on a 2-hour discharge/4-hour charge schedule contained 5.0 ampere-hours theoretical equivalents of zinc. The output per discharge during test cycling was to 2.6 and 3.0 ampere-hours or 52 and 60 percent zinc depth. Anodes that were subjected to 24-hour discharge/24-hour charge cycling contained 10 ampere-hours theoretical equivalents of zinc. The output per discharge of these cells was 7.5 ampere-hours or 75 percent zinc depth.

C. Membrane Separator

PERMION 110 separator was replaced with PERMION 1770C in the zinc-oxygen rechargeable unit cell. PERMION 110 was not available from the supplier, as was explained in the last quarterly report.

PERMION 1770C continues to demonstrate compatibility with the environment within the experimental unit cell. One layer of this material successfully resists dendrite penetration and oxygen permeation. There has not been a single incident of dendrite penetration observed, even in a cell that was subjected to abusive overcharge during instrument failure. Absolutely no evidence of degradation of this material has been observed in the environment to which it has been subjected in the unit cell. PERMION 1770C removed from the cells after testing appeared in near perfect condition. This material is a product of R.A.I. Research Corporation, formerly Radiation Applications Incorporated, and is reported to be chemically grafted polyethylene.

D. Rechargeable Unit Cell Performance at 25°C and 0°C

1. 2-Hour Discharge/4-Hour Charge of Unit Cells Employing Thin "fixed-zone" Oxygen Electrodes with 15 and 20 Ampere-Hour Zinc Gel Anodes

Cycling at 25°C of unit cells employing zinc gel anodes containing 15 and 20 ampere-hours of zinc capacity was continued. The purpose of these

*Electroformation consisted of charging the cells at 210 mA for 24 hours. This amounted to 5 ampere hours.

tests was to establish if anode slump due to shape change could be retarded and cycle life extended on zinc gel anodes. A 2-hour discharge at 22-25 mA/cm² (to 2.5 - 3.0 ampere-hours output) was equivalent to only 13-17 percent of the theoretical ampere-hour equivalents of zinc present in the anodes.

Cycle life of 10 ampere-hour cells was extended from 50-60 cycles to 176 cycles when the average depth of zinc discharge was decreased from 27 to 15 percent.

Figure 4 shows the performance of a unit cell employing a 15 ampere-hour zinc gel anode.

Figure 5 shows the performance of a unit cell employing a 20 ampere-hour zinc gel anode.

Figure 6 shows cycles delivered from a unit cell employing a 20 ampere-hour zinc gel anode. The cell delivered 51 cycles at 25°C, and was then transferred to 0°C at which it delivered 97 cycles.

2. 2-Hour Discharge/4-Hour Charge at 25°C of a Unit Cell Employing Thin "fixed-zone" Oxygen Electrodes and ZnO # 1 Anodes Formed to 5.0 Ampere-Hours Capacity

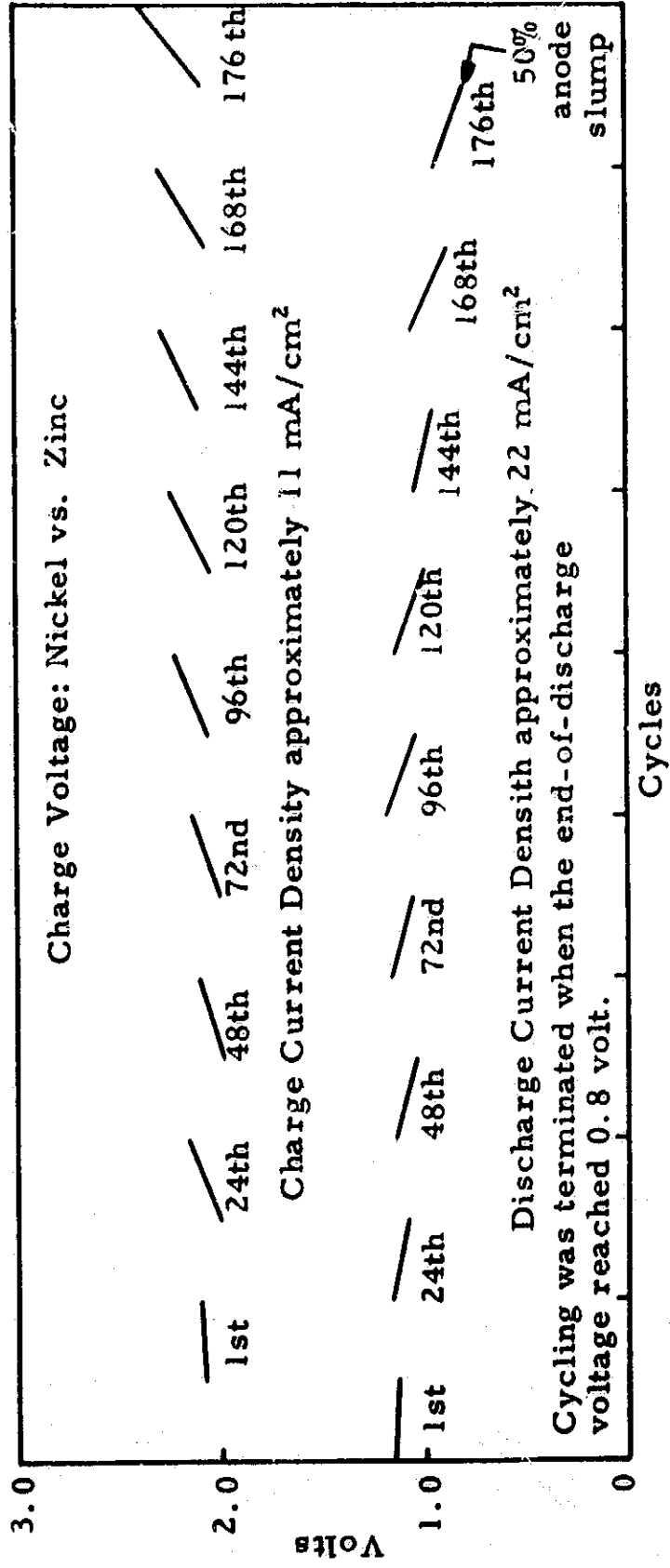
Unit cells employing anodes fabricated from the zinc oxide formulation designated ZnO #1 were formed to 5.0 ampere-hours before being subjected to test cycling on a 2-hour discharge/4-hour charge schedule.

Figure 7 shows 100 cycles delivered from a cell that was discharged across a fixed resistance of 0.75 ohm to 2.6 ampere-hours output or 52 percent zinc depth. The discharge current density was 27 mA/cm².

Figure 8 shows 144 cycles delivered by a cell discharged at 1.5 amperes (constant current) to 3.0 ampere-hours output or 60 percent zinc depth. The discharge current density was 31 mA/cm².

FIGURE 4
PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A 15 AMPERE-HOUR ZINC GEL ANODE

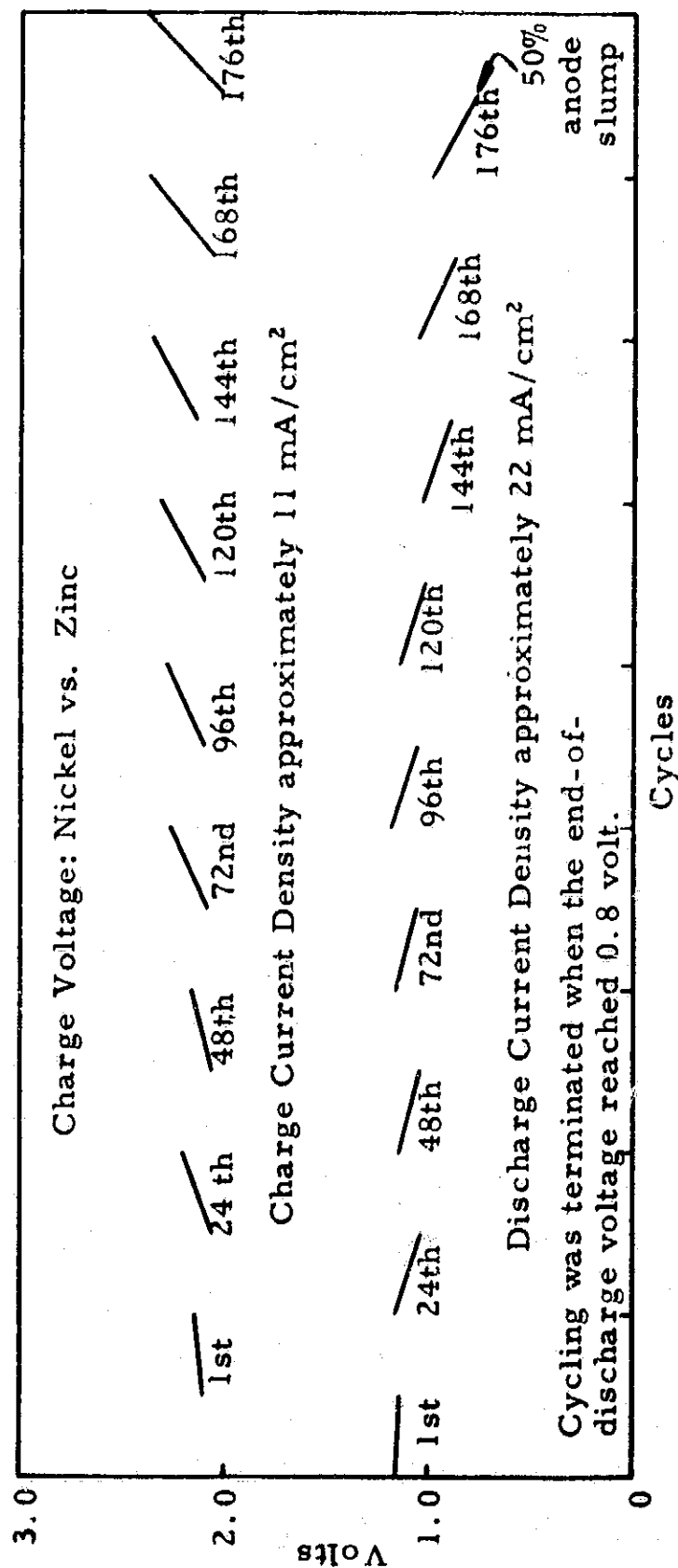
Theoretical Anode Depth of Discharge = 17%
2-Hour Discharge/4-Hour Charge at 25°C



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FIGURE 5
PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A 20 AMPERE-HOUR ZINC GEL ANODE

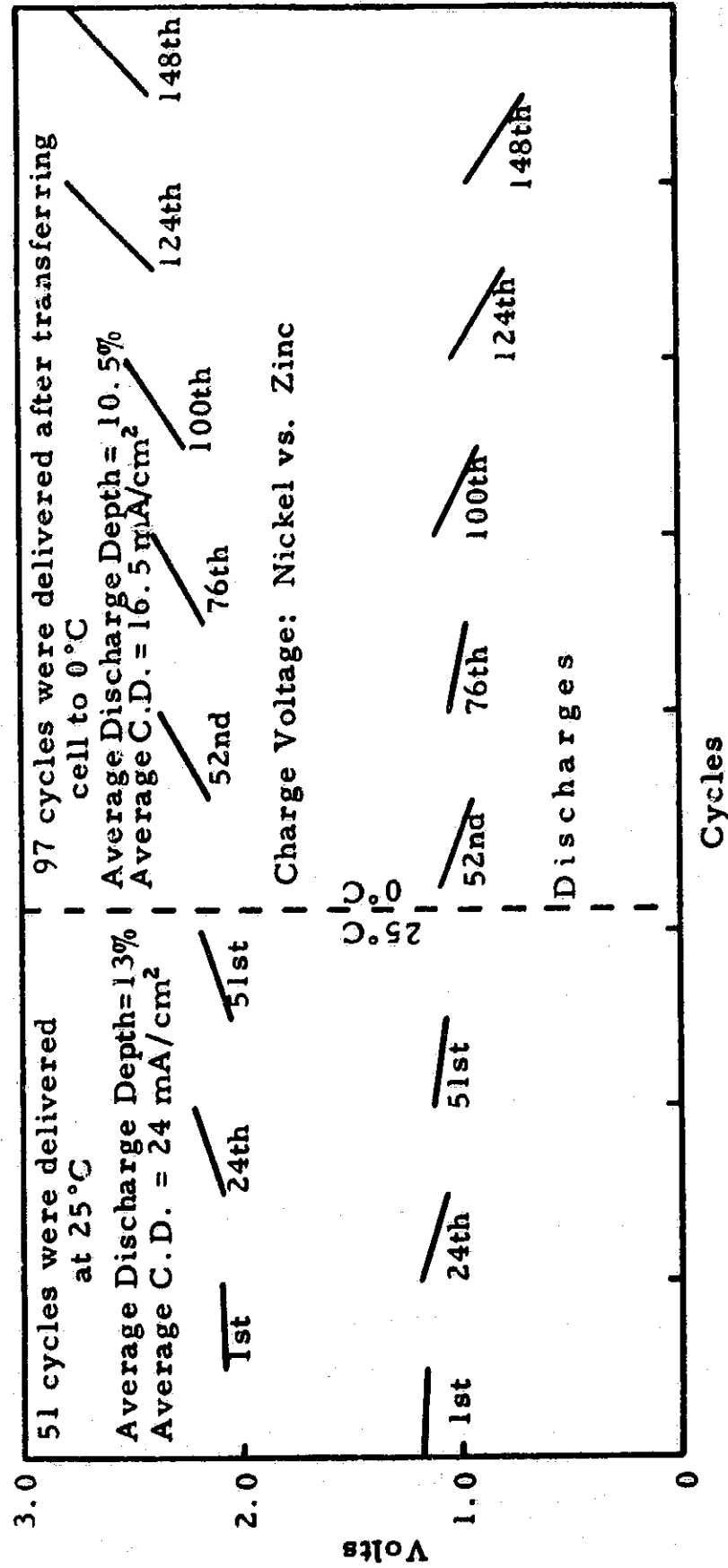
Theoretical Anode Depth of Discharge = 13%
2-Hour Discharge/4-Hour Charge at 25 °C



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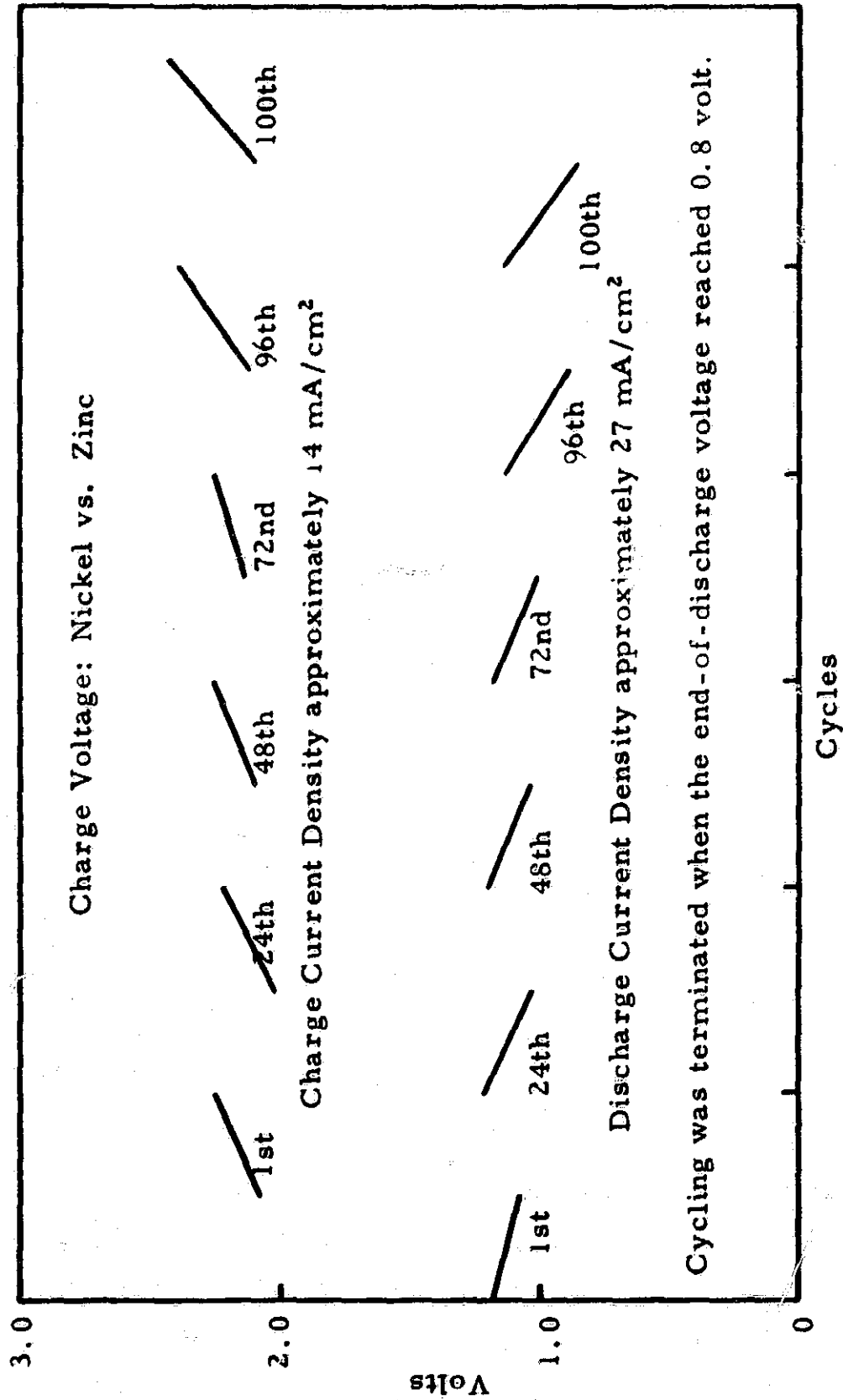
FIGURE 6
PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A 20 AMPERE-HOUR ZINC GEL ANODE

Discharge was across a fixed resistance of 0.75 ohm
Charge was constant current, balanced so the input was equal to the output
Cycling was conducted on a 2-hour discharge/4-hour charge schedule



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FIGURE 7
PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A 10 AMPERE-HOUR ZnO#1 ANODE
Theoretical Zinc Depth of Discharge 52%
2-Hour Discharge/4-Hour Charge at 25°C



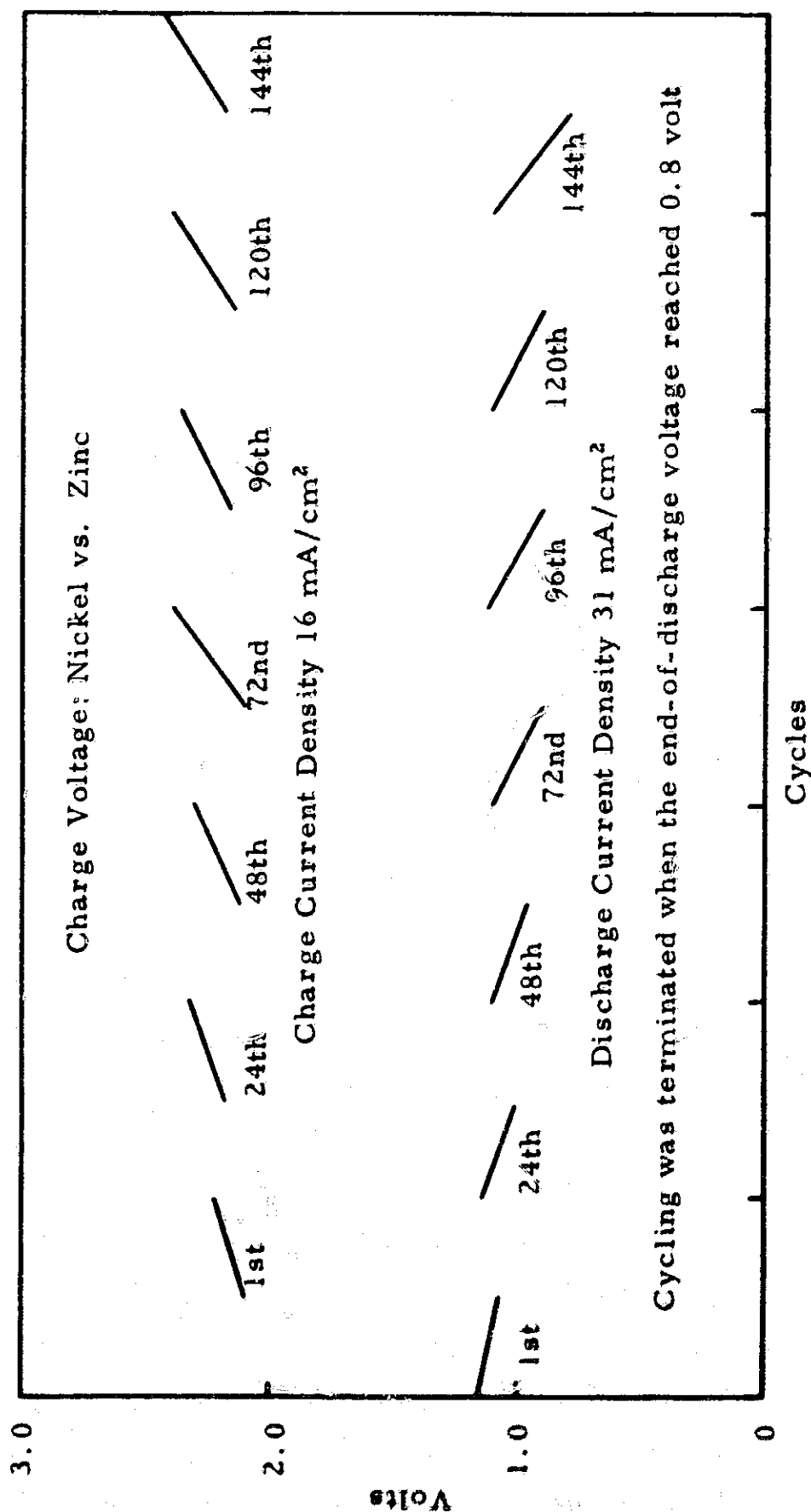
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FIGURE 8

PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"

OXYGEN ELECTRODE AND A 15 AMPERE-HOUR ZnO#1 ANODE

Theoretical Zinc Depth of Discharge 60%
2-Hour Discharge/4-Hour Charge at 25°C



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3. 2-Hour Discharge/4-Hour Charge at 25°C of a Unit Cell Employing a Thin "fixed-zone" Oxygen Electrode and ZnO #10 Anode Formed to 5.0 Ampere-Hours Capacity

Figure 9 shows 120 cycles delivered from a unit cell employing an anode fabricated from the formulation designated ZnO#10. This cell was formation charged to 5.0 ampere-hours before being subjected to 2-hour discharge/4-hour charge test cycling. Discharge was at 1.5 amperes (constant current) to 3.0 ampere-hours output or 60 percent zinc depth. The discharge current density was 31 mA/cm².

4. 2-Hour Discharge/22-hour Charge at 25°C of a Unit Cell Employing a Thin "fixed-zone" Oxygen Electrode and a ZnO #1 Anode Formed to 5.0 Ampere-Hours Capacity

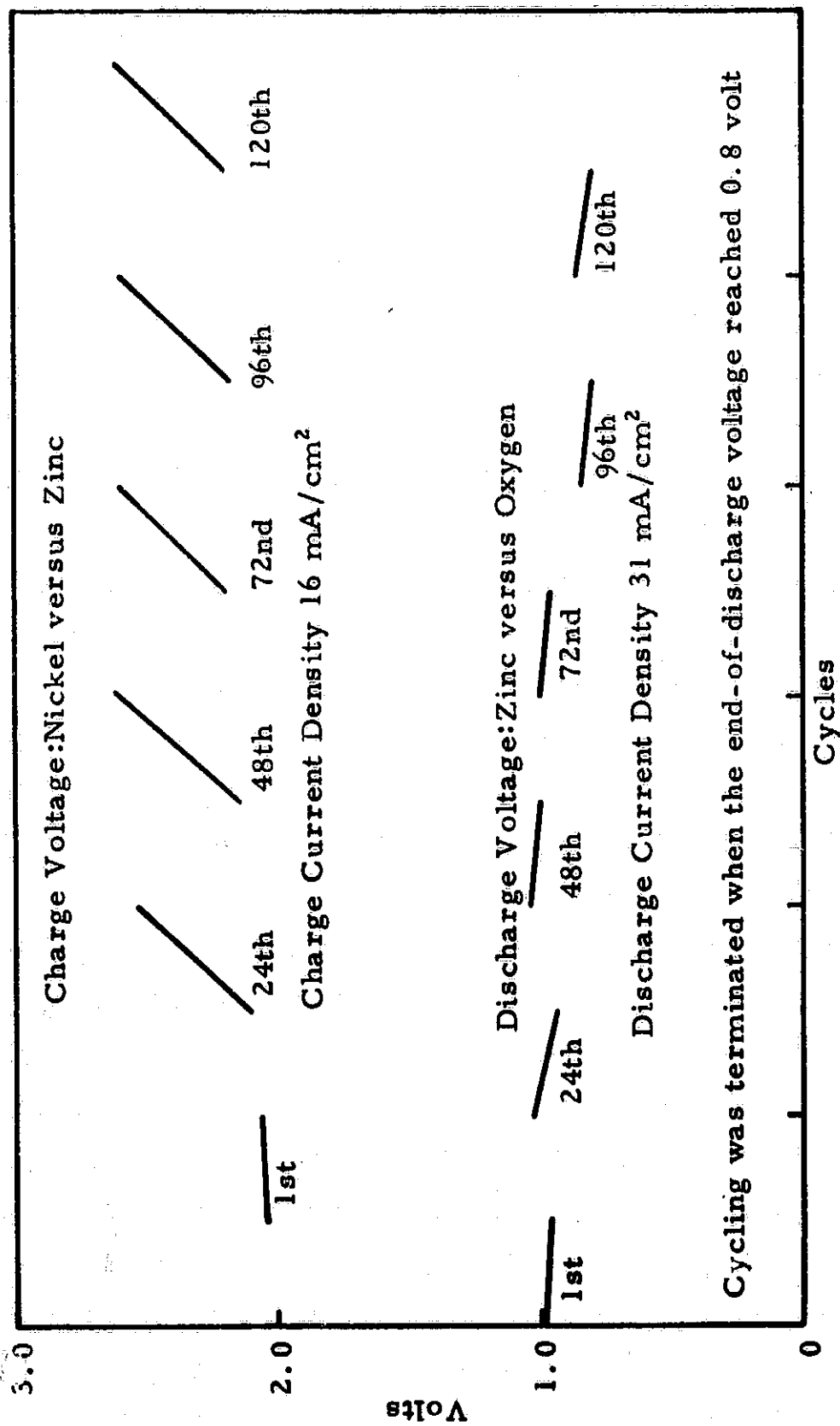
Figure 10 shows every eighth cycle of 40 cycles delivered by a unit cell that was formation-charged to 5.0 ampere-hours capacity before test cycling on a 2-hour discharge/22-hour charge schedule. The cell was discharged at 1.5 amperes (constant current) to a 3.0 ampere-hour output or 60 percent zinc depth. The discharge current density was 31 mA/cm².

5. Performance of Unit Cells at 0°, 25°, and 40°C Employing Thin "fixed-zone" Oxygen Electrodes and ZnO # 19 Anodes on a 24-Hour Discharge/24-Hour Charge Schedule

Unit cells employing anodes fabricated from a zinc oxide formulation designated ZnO #19 were formed to 10.0 ampere-hours capacity before being subjected to test cycling on a 24-hour discharge/24-hour charge schedule. Figures 11 and 12 show performance of unit cells cycled at 25°C and 40°C, respectively. The cells were discharged at 0.32 ampere (constant current) to 7.5 ampere-hours output or 75 percent zinc depth. The discharge current density was 6.6 mA/cm².

Figure 13 shows performance of an identical cell from which 10 discharges were delivered at 40°C on a 2-hour discharge/4-hour charge schedule, after which the cell was transferred to the 24-hour discharge/24-hour charge schedule at 0°C and 11 additional cycles were delivered.

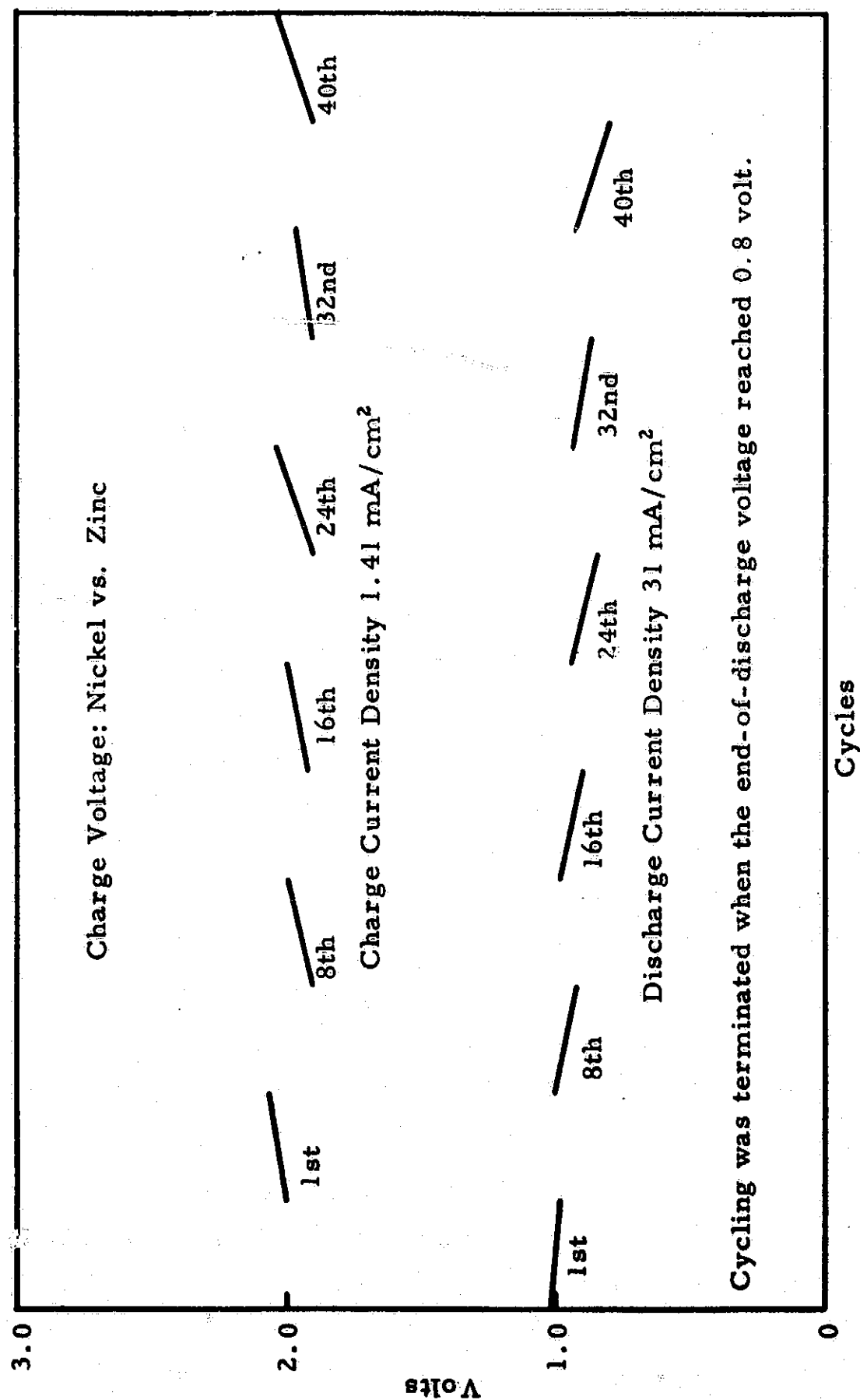
FIGURE 9
PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A 15 AMPERE-HOUR ZnO#10 ANODE
Theoretical Zinc Depth of Discharge 60%
2-Hour Discharge/4-Hour Charge at 25 °C



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FIGURE 10

PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A 15 AMPERE-HOUR ZnO#1 ANODE
Theoretical Zinc Depth of Discharge 60%
2-Hour Discharge/22-Hour Charge at 25°C

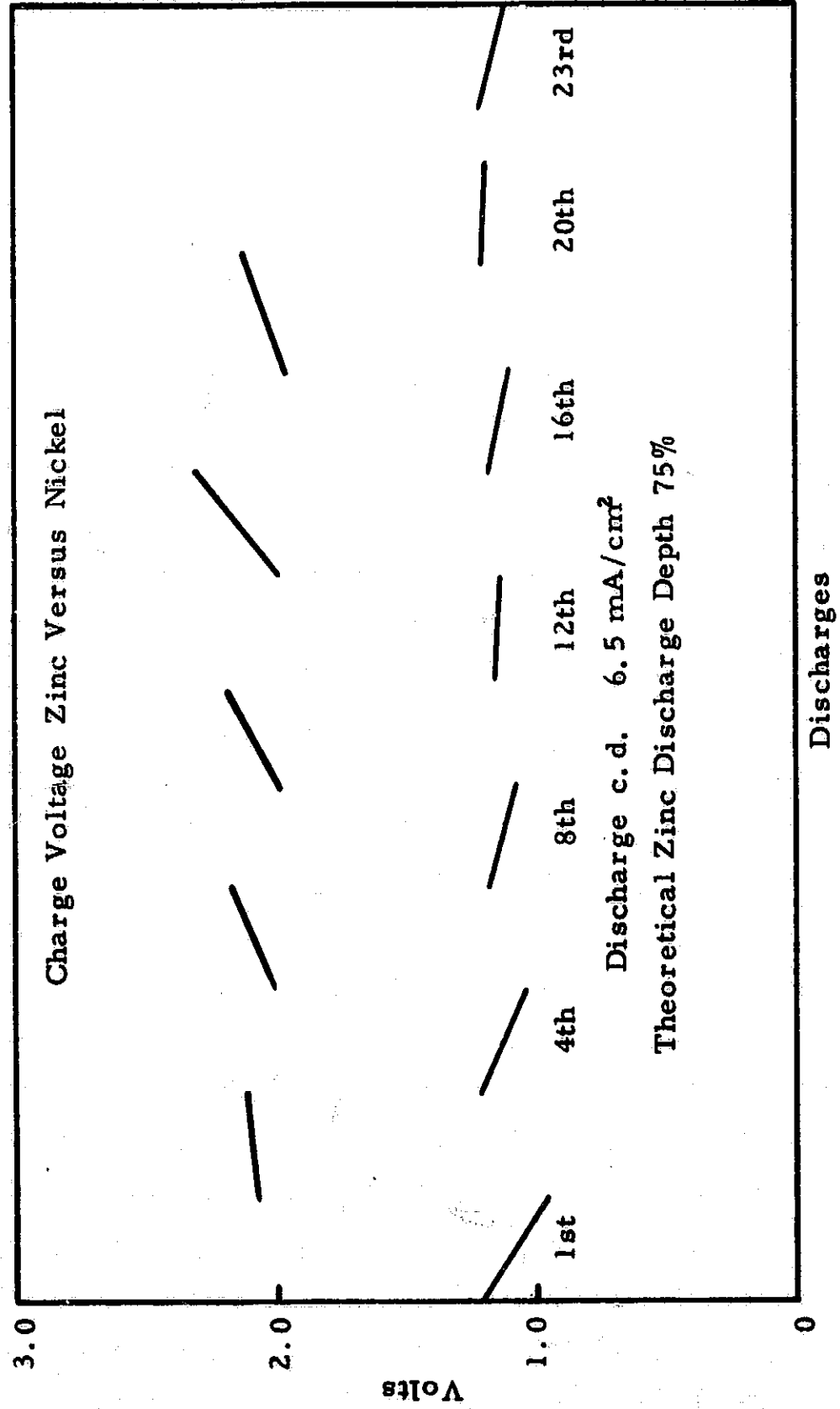


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FIGURE 11

DISCHARGE PERFORMANCE OF A UNIT CELL EMPLOYING A
THIN "FIXED-ZONE" OXYGEN ELECTRODE AND A ZnO# 19 ANODE

24-Hour Discharge/24-Hour Charge at 25 °C
Constant Current Discharge at 0.32 Ampere

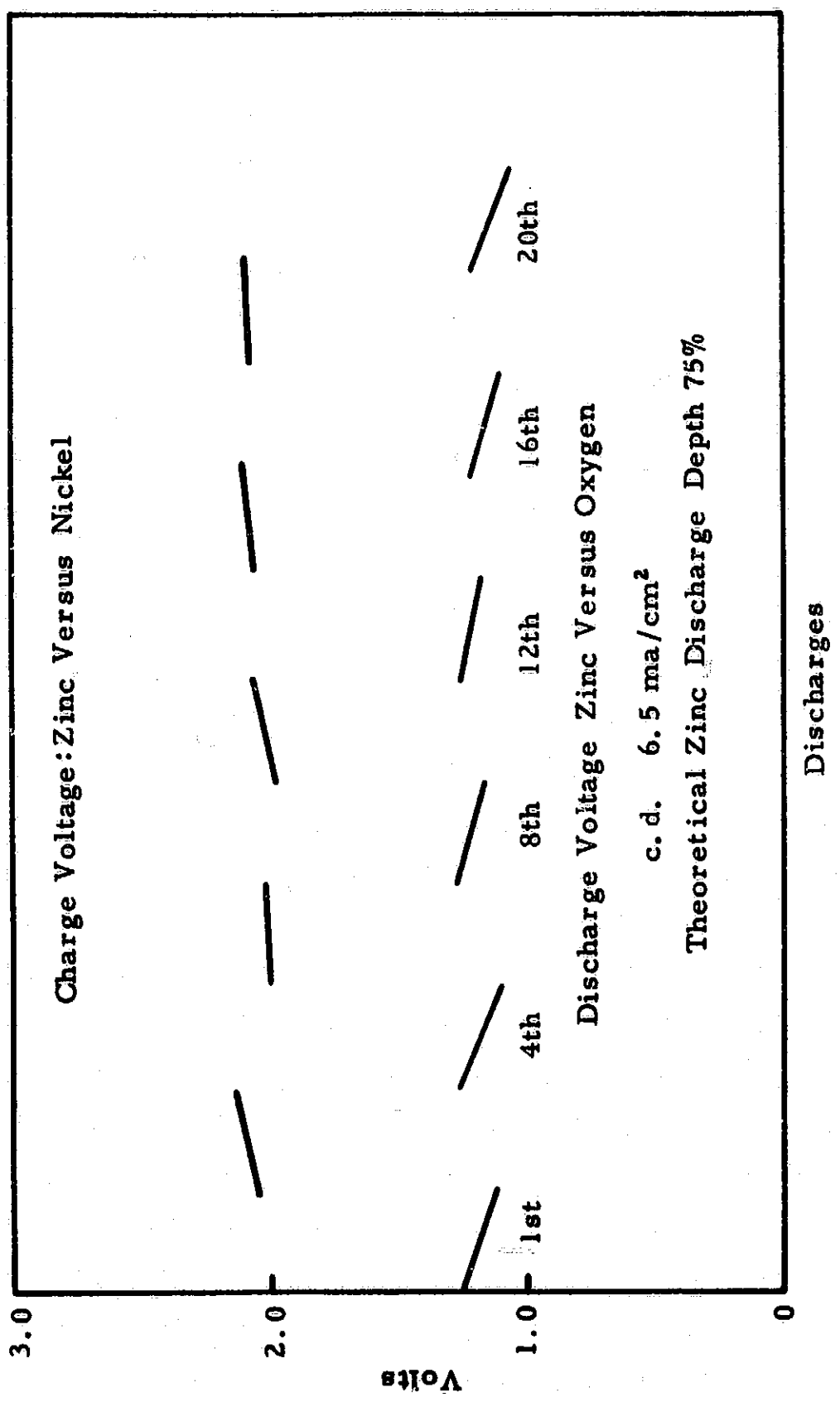


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FIGURE 12

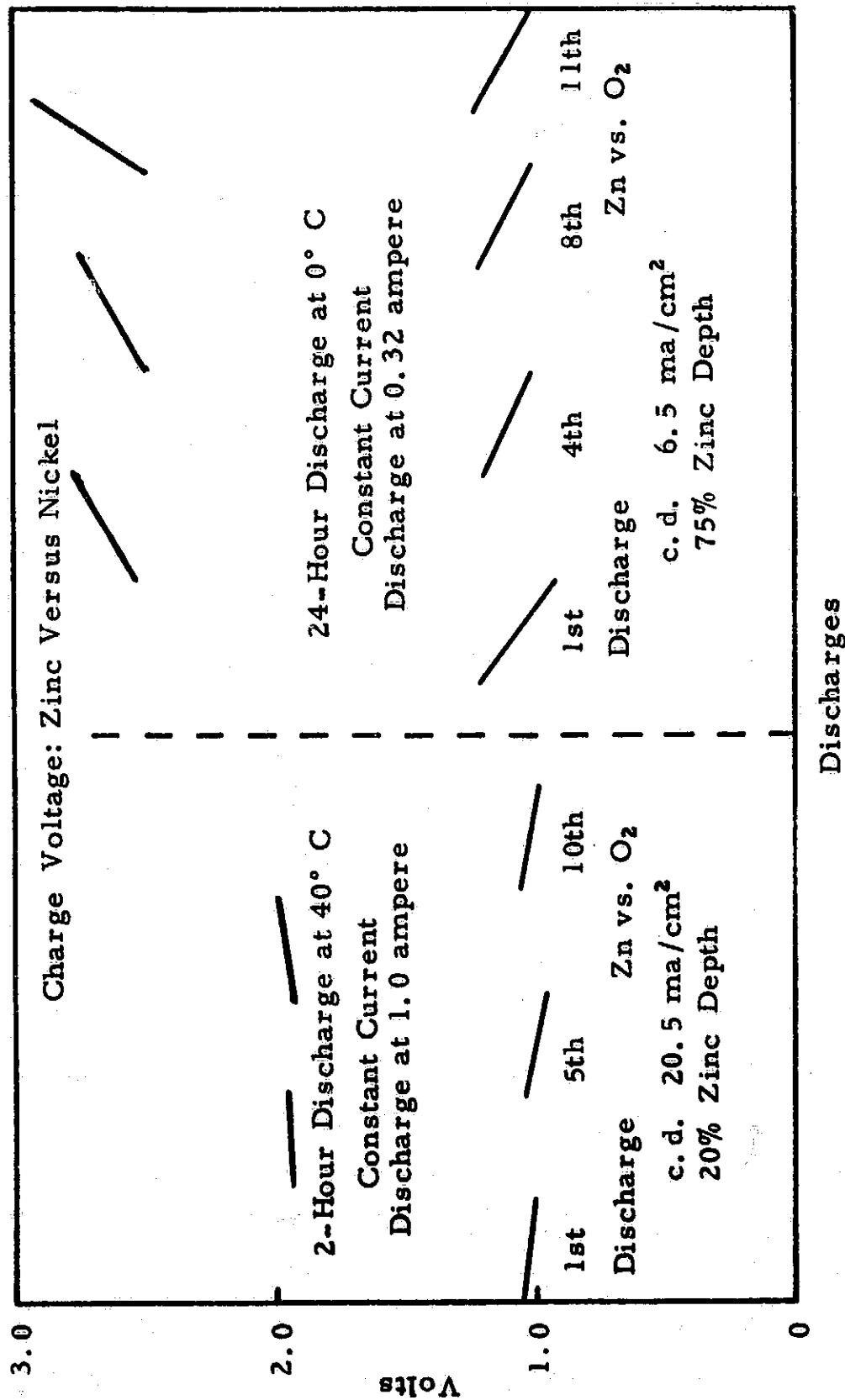
DISCHARGE PERFORMANCE OF A UNIT CELL EMPLOYING A
THIN "FIXED-ZONE" OXYGEN ELECTRODE AND A ZnO# 19 ANODE

24-Hour Discharge/24-Hour Charge at 40°C
Constant Current Discharge at 0.32 Ampere



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FIGURE 13
PERFORMANCE OF A UNIT CELL EMPLOYING A THIN "FIXED-ZONE"
OXYGEN ELECTRODE AND A ZnO#19 ANODE



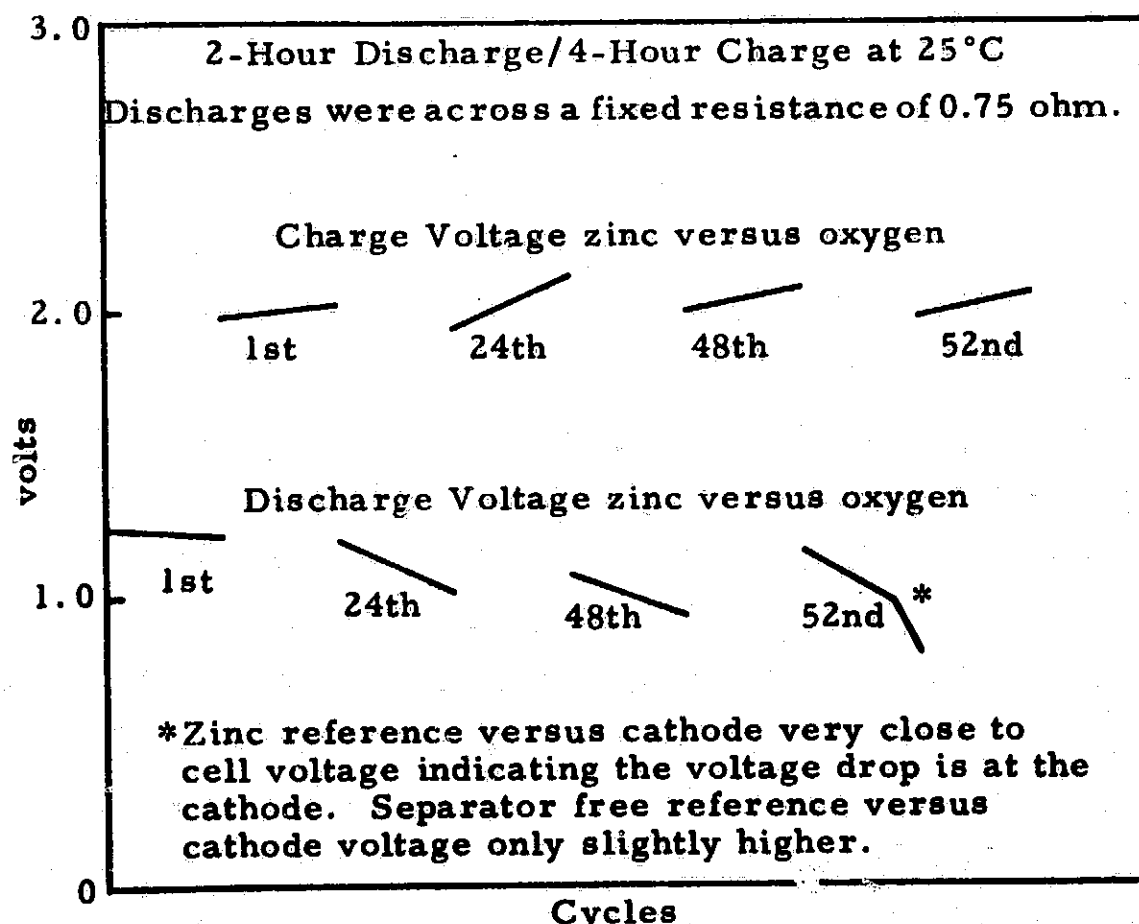
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6. 2-Hour Discharge/4-Hour Charge of a Unit Cell Employing an American Cyanamid LAB-40 Oxygen Electrode and a 20 Ampere-hour Zinc Gel Anode

It was demonstrated that cycle life could be extended to over 150 cycles with unit cells employing 15 and 20 ampere-hour zinc gel anodes and thin "fixed-zone" oxygen electrodes. To eliminate the anode as a limiting factor for at least 150 cycles, a cell was constructed with a 20 ampere-hour zinc gel anode and an American Cyanamid LAB-40 oxygen electrode. This cell was cycled under conditions identical to those under which a similar cell employing a thin "fixed-zone" oxygen electrode was cycled, and 52 cycles were delivered before deterioration of the active layer of the oxygen electrode was observed. The zinc was both charged and discharged against the LAB-40 oxygen electrode. The performance is shown in Figure 14.

FIGURE 14

PERFORMANCE OF A UNIT CELL EMPLOYING AN AMERICAN CYANAMID LAB-40 OXYGEN ELECTRODE AND A 20 AMPERE-HOUR ZINC GEL ANODE



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NEW TECHNOLOGY

There are no new technological advances falling within the scope of this contract to be reported during this period.

PROGRAM FOR THE NEXT REPORTING INTERVAL

The major portion of the work scheduled for the next reporting period will be devoted to the following:

- (a) The fabrication and shipment to NASA of two 6 volt-10 ampere-hour zinc-oxygen rechargeable batteries. These will include suitable pressure vessels for holding the required oxygen, electrolyte circulation systems, etc.
- (b) A design study to determine the energy density and projected design for a 28 volt-3 kWh rechargeable zinc-oxygen battery system based upon the best technology developed to date on this contract.
- (c) Preparation of the Final Report for Contract No. NAS-5-10247.

CONCLUSIONS AND RECOMMENDATIONS

A serious limitation to deep discharge of rechargeable zinc-oxygen batteries continues to be the redistribution of the zinc anode mass with successive cycling. For this reason, a comprehensive program directed toward the development of a configurationally stable rechargeable zinc electrode is recommended.

While the operational feasibility of the American Cyanamid LAB-40 electrode to serve both as a charging electrode and as an oxygen electrode has been demonstrated, this electrode cannot be recommended for such use at the present time. The main problem has been identified as being transport of the platinum catalyst to the zinc anode where a hydrogen gas couple is formed.

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